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Metal-Organic Material Polymer Coatings for Enhanced Gas Sorption Performance and Hydrolytic Stability Under Humid Conditions

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Supporting Information Placeholder

ABSTRACT: Physisorbent metal-organic materials (MOMs) have shown benchmark performance for highly selective CO_2 capture from bulk and trace gas mixtures. However, gas stream moisture can be detrimental to both adsorbent performance and hydrolytic stability. One of the most effective methods to solve this issue is to transform the adsorbent surface from hydrophilic to hydrophobic. Herein, we present a facile approach for coating MOMs with organic polymers to afford improved hydrophobicity and hydrolytic stability under humid conditions. The impact of gas stream moisture on CO_2 capture for the composite materials was found to be negligible under both bulk and trace CO_2 capture conditions with significant improvements in regeneration times and energy requirements.

KEYWORDS: *ultramicroporous materials, carbon dioxide, adsorption, separation, polymer coating*

INTRODUCTION

Carbon dioxide, CO_2, capture from trace (<2% CO_2) and bulk (>10% CO_2) gas mixtures will be a crucial technology in achieving carbon neutrality by 2050.[1] While clean technologies such as wind and solar power will play a major role in energy provision over the coming decades, increasing energy demands will dictate that fossil fuels will remain a key component of the global energy system into the second half of the century.[2] Additionally, trace concentrations of CO_2 are a significant impurity in industrial processes and can pose serious risks to human health in confined spaces such as spacecraft and submarines where access to fresh air is difficult.[3] CO_2 removal from natural gas (NG) is imperative to achieve pipeline quality and prevent freezing during liquefaction,[4] while prolonged human exposure to trace CO_2 concentrations (*ca.* 0.5% CO_2) can lead to headaches and drowsiness while elevated concentrations can lead to increased cardiac output and asphyxiation.[5, 6]

To date, carbon capture and sequestration (CCS) has been hampered by high costs (>100 US$/t CO_2 captured) and techno-economic uncertainties of liquid amine based CCS technologies.[7] In postcombustion-CO_2 capture during power generation, the CO_2 scrubbing process reduces the overall energy generation efficiency by up to 30%.[8] While traditional CCS technologies are suitable for large point sources producing bulk concentrations of CO_2, alternative approaches are required for mobile sources. Trace capture *via* direct air capture (DAC) of atmospheric CO_2 and confined space CO_2 control in submarines and spacecraft rely upon chemical absorption scrubbing technologies.[3, 9] Chemical fixation of CO_2 on CaO/LiOH *via* a reversible reaction gives way to the formation of metal carbonates. These scrubbing technologies are limited by poor sorption kinetics, energy-intensive regeneration, and reduced performance with cycling.[10] The limitations of traditional CO_2 scrubbers have accelerated the development of a new generation CO_2 capture technologies. Adsorption has long been touted as an energy efficient alternative to traditional liquid amine-based technologies.[11, 12] Traditional adsorbents such as zeolites have been used in the petrochemical industry for decades; however, these materials are hampered by issues such as low selectivity and high regeneration energies.[13-15]

The demand for energy-efficient solutions to CO_2 capture has spurred research into porous Metal-Organic Materials (MOMs),[16] also known as Porous Coordination Polymers (PCPs),[17] or Metal–Organic Frameworks (MOFs).[18, 19] MOMs are a class of porous adsorbents that offer paradigm shift in a wide range of applications such as of carbon capture and energy efficient gas purifications.[12, 20-22] The tuneable nature of MOMs has enabled improvements in terms of uptake capacities, CO_2 selectivity and interaction energy compared to classical adsorbent materials.[23] Despite these improvements, many MOMs suffer from reduced performance and hydrolytic instability in the presence of moisture.[14, 24-26] Improvements in CO_2-adsorbent interactions generally gives way to increased H_2O uptake, while improved hydrophobicity tends to reduce CO_2 sorption performance.[27] Additionally, traditional approaches to improving the stability of MOMs toward water or humidity gives way to reduced porosity and often involves

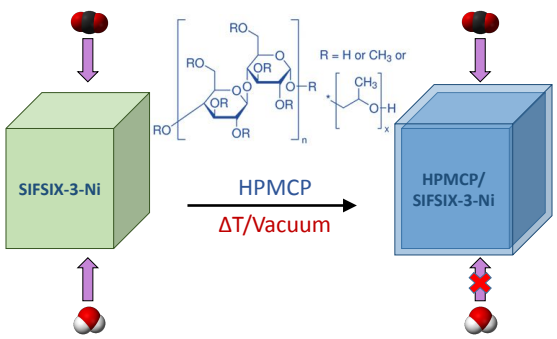

Figure 1. Illustration of HPMCP-coating on the surface of **SIFSIX-3-Ni** and the improvement of moisture resistance.

complex synthesis.[28, 29] Therefore, it is imperative to develop

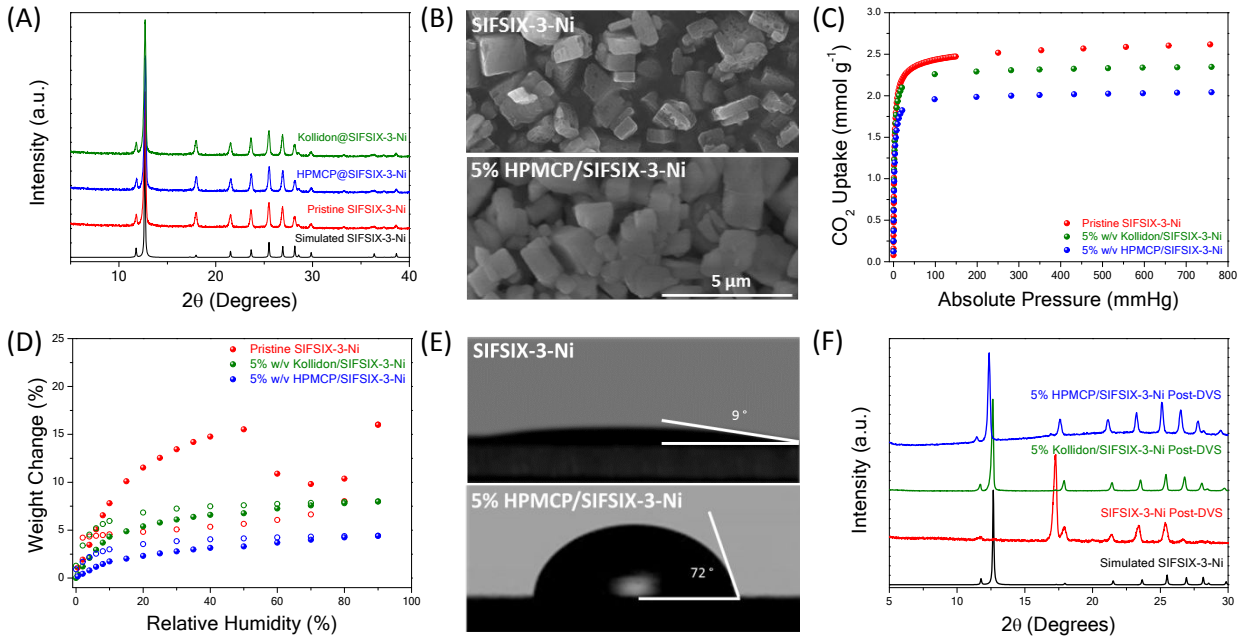

Figure 2. (A) PXRD patterns of pristine and polymer coated **SIFSIX-3-Ni**. (B) SEM images of (Top) pristine and (Bottom) HPMCP coated **SIFSIX-3-Ni**. (C) Low pressure CO_2 adsorption isotherms for pristine and polymer coated **SIFSIX-3-Ni** at 298 K. (D) DVS H_2O sorption/desorption isotherms for pristine and polymer coated **SIFSIX-3-Ni** at 308 K. (E) Water contact angle analysis of (Top) pristine and (Bottom) HPMCP coated **SIFSIX-3-Ni**. (F) post-DVS PXRD patterns of pristine and polymer coated **SIFSIX-3-Ni**.

facile approaches towards humidity stability while maintaining adsorbent performance.

Recently, the use of hydrophobic polymer coatings has been shown to improve hydrolytic stability of MOMs in the presence of moisture.[30-39] Indeed, polymer/MOM composites have been studied as membrane materials[40-43] and the use of hydrophobic polymer coating in formulation of hygroscopic pharmaceutical ingredients is commonplace.[44] Herein, we report a general approach for a polymer-coating treatment to form a hydrophobic film upon the surface of MOMs for improved hydrolytic stability and gas sorption performance under humid conditions (Fig. 1). To demonstrate the effectiveness of this polymer-coating approach, **SIFSIX-3-Ni** $\{[Ni^{2+}(pyz)_2(SiF_6^{2-})]_n\}$[25, 45] a benchmark MOM for CO_2 capture was chosen for study. **SIFSIX-3-Ni** is a member of a subclass of MOMs known as Hybrid Ultramicroporous Materials (HUMs)[46] that combine ultramicropores with a strong electrostatic contribution *via* inorganic anions within the pore channels. HUMs have previously been found to show exceptional gas separation performance for multiple dry and wet gas mixtures.[47-53] **SIFSIX-3-Ni** was coated with two polymers, HPMCP HP-55 and Kollidon SR (Fig. S26). HPMCP HP-55 is widely used as an enteric coating agent by the pharmaceutical industry due to its film formation strength and high acid resistance properties. Kollidon SR is inert i.e. contains no ionic groups and can produce a very coherent hydrophobic matrix. These polymers were chosen due to their widespread availability and hydrophobic properties which are commonly used to improve the hydrolytic stability of pharmaceutical formulations. The performance of all materials was evaluated using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), dynamic vapour sorption (DVS), water contact angle (WCA), scanning electron microscopy (SEM), single-component and mixed gas adsorption and gravimetric gas uptake experiments. To the best of our knowledge, this is the first work that improves the CO_2 sorption performance of MOMs from both trace (1% CO_2) and bulk (15% CO_2) gas mixtures under humid conditions using hydrophobic polymer coatings.

RESULTS AND DISCUSSION

SIFSIX-3-Ni was synthesised *via* a slurrying method as previously reported (See Supporting Information†).[25] To facilitate coating of **SIFSIX-3-Ni**; 1, 2 and 5 wt.% HPMCP HP-55 and Kollidon SR solutions were prepared by dissolving polymer in MeOH with the aid of ultrasonication. 0.1 g of sieved **SIFSIX-3-Ni** particles (75 - 100 µm), were added to glass vials containing 5 ml of prepared polymer solutions. Coating of **SIFSIX-3-Ni** samples was conducted in a lab shaker, by subjecting the mixtures to agitation for 30 min. Polymer coated samples of **SIFSIX-3-Ni** (Denoted **HPMCP/SIFSIX-3-Ni** and **Kollidon/SIFSIX-3-Ni**) were collected *via* vacuum filtration, followed by aging at 40 °C for a period of 24 h. Finally, all samples were fully activated by heating to 100 °C under vacuum for 8 h. The hydrophobic coating is formed through combination of hydrogen bonds and π–π stacking between the MOM and the Kollidon SR and HPMCP polymers.[35,44,54]

The morphology, crystallinity and thermal stability of pristine and coated **SIFSIX-3-Ni** samples were investigated using SEM, PXRD and TGA, respectively. SEM images show that pristine **SIFSIX-3-Ni** crystals have regular cubic morphology and a smooth surface (Fig. 2B). Similarly, the HPMCP and Kollidon coated **SIFSIX-3-Ni** samples exhibit similar morphology and a characteristically smooth surface. TEM images (Fig. S27) also display a cubic morphology for HPMCP coated **SIFSIX-3-Ni**, however, there was no obvious presence of a polymer coating observed. From PXRD results, there was no notable differences observed between the pristine and polymer-coated **SIFSIX-3-Ni** samples (Fig. 2A, S1-S2). The crystalline structures of the **SIFSIX-3-Ni** materials were maintained after the coating process. TGA was used to analyse the thermal stability of both pristine and polymer coated **SIFSIX-3-Ni** (Fig. S5). There were notable differences in terms

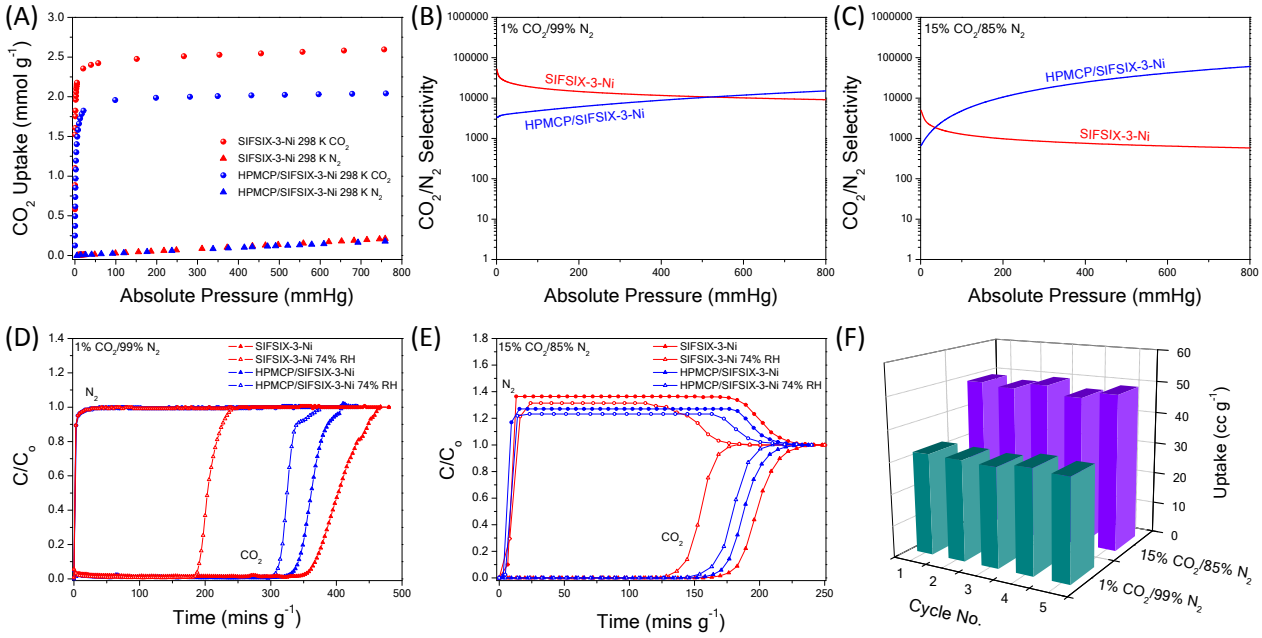

Figure 3. (A) Single component gas sorption isotherms (CO_2 & N_2) for pristine and polymer coated **SIFSIX-3-Ni** at 298 K. (B) 1% CO_2/99% N_2 and (C) 15% CO_2/85% N_2 IAST selectivity plots for pristine and polymer coated **SIFSIX-3-Ni** at 298 K. (D) 1% CO_2/99% N_2 and (E) 15% CO_2/85% N_2 dry and 74% RH gas mixture breakthrough curves for coated and uncoated **SIFSIX-3-Ni**. (F) **HPMCP/SIFSIX-3-Ni** recyclability tests for humid 1% CO_2/99% N_2 and 15% CO_2/85% N_2 gas mixtures (Regeneration at 80 °C).

of the decomposition profiles observed during thermal analysis. **SIFSIX-3-Ni** displayed *ca.* 20 wt. % weight loss at 120 °C which can be attributed to water loss, this was roughly halved through the incorporation of Kollidon and HPMCP coatings. All three samples displayed similar weight losses above 200 °C suggesting that the decomposition temperatures of the HPMCP and Kollidon coatings occur at similar temperatures to those of the crystalline MOM.

To examine the effects of coating upon the porosity of polymer-MOM composites, single component gas adsorption isotherms of the pristine and polymer coated **SIFSIX-3-Ni** samples were collected for CO_2 and N_2 (Fig. 2C & 3A) at 298 K. The CO_2 and N_2 uptake observed for the pristine **SIFSIX-3-Ni** (*ca*. 2.5 & 0.3 mmol/g at 1 bar, respectively) are consistent with previous reports.[25] The HPMCP and Kollidon coated **SIFSIX-3-Ni** samples were found to have reduced saturation CO_2 uptake compared to the pristine samples (Fig. 2C). Upon introduction of varying wt. % (1, 2 and 5 wt. %) of HPMCP and Kollidon during the coating process there is a noticeable reduction in saturation CO_2 uptake. The reduction in CO_2 uptake for polymer coated **SIFSIX-3-Ni** was found to correspond to the increased levels of polymer coating (Figs. S6-S8, S29). A similar trend was observed for N_2 uptake for HPMCP coated **SIFSIX-3-Ni** (Fig. 3A).

After fitting using the Dual-site Langmuir-Freundlich (DSLF) model, analysis of the pure component isotherms *via* ideal adsorbed solution theory (IAST)[55] allowed us to estimate the CO_2/N_2 selectivity (S_{CN}) under relevant conditions for trace and bulk CO_2 capture (CO_2 mole fractions of 0.01 and 0.15) for both pristine and HPMCP coated **SIFSIX-3-Ni** (Fig. 3B & 3C). **SIFSIX-3-Ni** exhibited benchmark S_{CN} for both trace (S_{CN} = 9132) and bulk (S_{CN} = 581) gas mixtures. Interestingly, the addition of polymer coatings was found to increase S_{CN} for HPMCP coated **SIFSIX-3-Ni** materials for both trace (S_{CN} = 15070) and bulk (S_{CN} = 60650) gas mixtures. The exceptionally high S_{CN} values exhibited by HPMCP coated **SIFSIX-3-Ni** suggest its potential for CO_2/N_2 separations relevant to indoor air quality control (1/99 *v/v*) and post combustion CO_2 capture (15/85 *v/v*).

To further examine the CO_2 sorption performance of composite materials, kinetics studies were performed on both pristine and HPMCP coated **SIFSIX-3-Ni** (Fig. S23-S25). Activated samples of both pristine and polymer coated **SIFSIX-3-Ni** were exposed to a constant flow of 0.01, 0.15 and 1.0 bar CO_2 at 308 K. There was a notable correlation between kinetic uptake performance and CO_2 partial pressure for all materials examined. At 1.0 bar CO_2, *ca.* 90% saturation was achieved in < 1 min for all samples. Conversely, for 0.01 bar CO_2, *ca*. 2 h was required to achieve saturation uptake. Saturation uptakes and kinetic uptake rates were found to be consistent for all materials, suggesting that the presence of a polymer layer has little impact upon the uptake kinetics of composite adsorbents.

To investigate the H_2O sorption properties of the pristine and polymer coated **SIFSIX-3-Ni**, DVS experiments were carried out (Fig. 2D). Pristine **SIFSIX-3-Ni** exhibits a characteristic negative water sorption isotherm.[56] The negative adsorption is attributed to a water-induced phase change from a porous **puck** topology to a nonporous **sql** topology, however, the **pcu** topology is recoverable by heating under vacuum. Conversely, both HPMCP and Kollidon coated **SIFSIX-3-Ni** exhibit fully reversible H_2O sorption isotherms. The introduction of HPMCP and Kollidon during the coating procedure gave way to a reduction in the saturation H_2O uptake (4.4 & 7.9 wt.%, respectively) compared to the pristine **SIFSIX-3-Ni** (16 wt.%). The lower H_2O uptake observed for HPMCP coated SIFSIX-3-Ni can be attributed to a higher density of -CH_3 functional groups in the HPMCP coated polymer compared to Kollidon SR (Fig. S26). Post-sorption PXRD demonstrated that the **pcu** network of **SIFSIX-3-Ni** was maintained upon exposure to H_2O during DVS experiments on the polymer coated samples (Fig. 2F). To further examine surface hydrophobicity, WCA measurements were performed on pelletized pristine and HPMCP coated **SIFSIX-3-Ni** (Fig. 2E).

HPMCP coated **SIFSIX-3-Ni** was chosen for further testing due to the lower H_2O uptake compared to Kollidon coated **SIFSIX-3-Ni** composite. The HPMCP coated sample exhibited an 8-fold increase in WCA compared to uncoated **SIFSIX-3-Ni** (72° vs. 9°, respectively). The addition of a polymer coating imparts improved hydrophobicity and stability upon **SIFSIX-3-Ni**.

To examine the gas separation performance of polymer coated MOMs, experimental breakthrough studies were performed on both pristine and HPMCP coated **SIFSIX-3-Ni** for CO_2/N_2 (1/99 and 15/85 *v/v*) gas mixtures at room temperature under both dry and humid conditions (Fig. 3D & 3E). As illustrated in Fig. 3D and 3E, efficient CO_2/N_2 separation was achieved for pristine and polymer coated **SIFSIX-3-Ni** for both trace and bulk dry mixed gas streams. N_2 gas was eluted through the bed immediately, whereas CO_2 was retained in the adsorbent bed. For 15/85 CO_2/N_2 gas mixtures, pristine and HPMCP coated **SIXSIX-3-Ni** were found to achieve CO_2 uptake capacities of 2.4 and 2.2 mmol g^{-1}, respectively. For 1/99 CO_2/N_2 gas mixtures, uptakes of 1.7 and 1.5 mmol g^{-1}, respectively, were observed. Upon exposure to humid (74% RH) trace and bulk gas mixtures, **SIFSIX-3-Ni** exhibited significant reductions in CO_2 sorption performance for both trace (47%) and bulk (22%) gas mixtures compared with those observed under dry conditions. Conversely, HPMCP coated **SIFSIX-3-Ni** performance was maintained under humid conditions with only minimal reductions in performance observed for trace (9%) and bulk (5%) gas mixtures. The performance of the pristine and polymer coated **SIFSIX-3-Ni** samples was found to be in agreement with those of the IAST predicted uptakes (Fig. S30-32). Temperature-programmed desorption (Fig. S21 & S22) illustrated that facile regeneration could be achieved due to a dramatic reduction in adsorbed H_2O during adsorption studies. Comparison with previously reported materials shows that HPMCP coated **SIFSIX-3-Ni** demonstrates benchmark CO_2 sorption performance (Table S3). The CO_2 removal performance of HPMCP coated **SIFSIX-3-Ni** combined with its recyclability (Fig. 3F) and stability (Fig. S28),[25] suggests that this material could be effectively employed for CO_2 removal from humid gas streams regardless of the CO_2 concentration.

CONCLUSIONS

In conclusion, efficient CO_2 capture can be achieved using physisorbent materials, however, the presence of moisture in the gas stream can have a detrimental effect upon performance. The inclusion of polymer coatings was employed to overcome the effects of moisture upon MOM performance. SEM and PXRD illustrated that the **SIFSIX-3-Ni** structure was unaffected during the polymer coating process, while single-component gas sorption isotherms illustrated that porosity remained intact. DVS and WCA analysis illustrated improved hydrophobicity, while dynamic gas breakthrough testing demonstrated that gas separation performance could be maintained under humid conditions using polymer coatings. Notably, the HPMCP coated **SIFSIX-3-Ni** maintained its characteristic **pcu** network upon prolonged exposure to moisture, overcoming conversion to the previously reported **sql** topology. This work illustrates how polymer-coatings impart improved hydrophobicity and gas separation performance upon MOM materials under humid conditions. This facile approach to adsorbent processing may provide a roadmap towards future use of MOMs in challenging industrial applications such as indoor air quality control and post combustion carbon capture.

ASSOCIATED CONTENT

Supporting Information

Experimental section, supplementary table and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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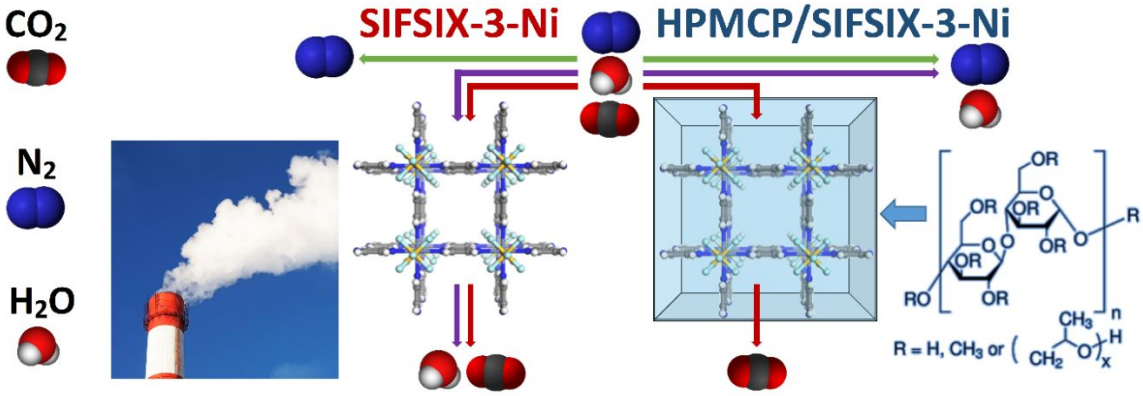
REFERENCES

1. Hulme, M., 1.5 °C and Climate Research after the Paris Agreement. *Nat. Clim. Change* **2016,** *6* (3), 222.
2. Odenberger, M.; Johnsson, F., Pathways for the European Electricity Supply System to 2050—The Role of CCS to Meet Stringent CO_2 Reduction Targets. *Int. J. Greenh. Gas Cont.* **2010,** *4* (2), 327-340.
3. Carey, R.; Gomezplata, A.; Sarich, A., An Overview Into Submarine CO_2 Scrubber Development. *Ocean Eng.* **1983,** *10* (4), 227-233.
4. Madden, D. G.; O'Nolan, D.; Chen, K.-J.; Hua, C.; Kumar, A.; Pham, T.; Forrest, K. A.; Space, B.; Perry, J. J.; Khraisheh, M.; Zaworotko, M. J., Highly Selective CO_2 Removal for One-Step Liquefied Natural Gas Processing by Physisorbents. *Chem. Commun.* **2019,** *55* (22), 3219-3222.
5. Scott, J. L.; Kraemer, D. G.; Keller, R. J., Occupational Hazards of Carbon Dioxide Exposure. *J. Chem. Heal. . Safe.* **2009,** *16* (2), 18-22.
6. OSHA Carbon Dioxide. Https://Www.Osha.Gov/Dts/Chemicalsampling/Data/CH_225400.Html.
7. Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Mac Dowell, N.; Fernández, J. R.; Ferrari, M.-C.; Gross, R.; Hallett, J. P., Carbon Capture and Storage Update. *Energ. Environ. Sci.* **2014,** *7* (1), 130-189.

8. Goto, K.; Yogo, K.; Higashii, T., A Review of Efficiency Penalty in a Coal-Fired Power Plant with Post-Combustion CO_2 Capture. *Appl. Energ.* **2013,** *111*, 710-720.
9. Hoffman, J. S.; Pennline, H. W. *Study Of Regenerable Sorbents for CO_2 Capture*; National Energy Technology Laboratory, Pittsburgh, PA (United States): 2001.
10. Bhatt, P. M.; Belmabkhout, Y.; Cadiau, A.; Adil, K.; Shekhah, O.; Shkurenko, A.; Barbour, L. J.; Eddaoudi, M., A Fine-Tuned Fluorinated MOF Addresses the Needs for Trace CO_2 Removal and Air Capture Using Physisorption. *J. Am. Chem. Soc.* **2016,** *138* (29), 9301-9307.
11. D'Alessandro, D. M.; Smit, B.; Long, J. R., Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chem. Int. Ed.* **2010,** *49* (35), 6058-6082.
12. Sumida, K.; Rogow, D. L.; Mason, J. A.; Mcdonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R., Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2011,** *112* (2), 724-781.
13. Merel, J.; Clausse, M.; Meunier, F., Experimental Investigation on CO_2 Post–Combustion Capture by Indirect Thermal Swing Adsorption Using 13X and 5A Zeolites. *Ind. Eng. Chem. Res.* **2008,** *47* (1), 209-215.
14. Mason, J. A.; McDonald, T. M.; Bae, T.-H.; Bachman, J. E.; Sumida, K.; Dutton, J. J.; Kaye, S. S.; Long, J. R., Application of a High-Throughput Analyzer in Evaluating Solid Adsorbents for Post-Combustion Carbon Capture via Multicomponent Adsorption of CO_2, N_2, and H_2O. *J. Am. Chem. Soc.* **2015,** *137* (14), 4787-4803.
15. Oschatz, M.; Antonietti, M., A Search for Selectivity to Enable CO_2 Capture with Porous Adsorbents. *Energ. Environ. Sci.* **2018,** *11* (1), 57-70.
16. Perry IV, J. J.; Perman, J. A.; Zaworotko, M. J., Design and Synthesis ff Metal–Organic Frameworks using Metal–Organic Polyhedra as Supermolecular Building Blocks. *Chem. Soc. Rev.* **2009,** *38* (5), 1400-1417.
17. Kitagawa, S.; Kitaura, R.; Noro, S. I., Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* **2004,** *43* (18), 2334-2375.
18. Farrusseng, D., *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*. John Wiley & Sons: 2011.
19. Macgillivray, L., Metal-Organic Frameworks: Design and Applications, John Wiley & Sons. Inc: 2010.
20. Li, J.-R.; Kuppler, R. J.; Zhou, H.-C., Selective Gas Adsorption and Separation in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009,** *38* (5), 1477-1504.
21. Shekhah, O.; Liu, J.; Fischer, R.; Wöll, C., MOF Thin Films: Existing and Future Applications. *Chem. Soc. Rev.* **2011,** *40* (2), 1081-1106.
22. Wang, C.; Liu, X.; Demir, N. K.; Chen, J. P.; Li, K., Applications of Water Stable Metal–Organic Frameworks. *Chem. Soc. Rev.* **2016,** *45* (18), 5107-5134.
23. Zhang, Z.; Tao, J.; Xiang, S.; Chen, B.; Zhou, W., New Progress of Microporous Metal–Organic Frameworks in CO_2 Capture and Separation. *Materials And Processes for CO_2 Capture, Conversion, and Sequestration* **2018**, 112.
24. Kumar, A.; Hua, C.; Madden, D. G.; O'Nolan, D.; Chen, K.-J.; Keane, L.-A. J.; Perry IV, J. J.; Zaworotko, M. J., Hybrid Ultramicroporous Materials (HUMs) with Enhanced Stability and Trace Carbon Capture Performance. *Chem. Commun.* **2017,** *53* (44), 5946-5949.
25. Kumar, A.; Madden, D. G.; Lusi, M.; Chen, K. J.; Daniels, E. A.; Curtin, T.; Perry IV, J. J.; Zaworotko, M. J., Direct Air Capture of CO_2 by Physisorbent Materials. *Angew. Chem. Int. Ed.* **2015,** *54* (48), 14372-14377.
26. Madden, D. G.; Scott, H. S.; Kumar, A.; Chen, K.-J.; Sanii, R.; Bajpai, A.; Lusi, M.; Curtin, T.; Perry IV, J. J.; Zaworotko, M. J., Flue-Gas And Direct-Air Capture of CO_2 by Porous Metal–Organic Materials. *Phil. Trans. A* **2017,** *375* (2084), 20160025.
27. Wang, Y.; Hu, Z.; Kundu, T.; Cheng, Y.; Dong, J.; Qian, Y.; Zhai, L.; Zhao, D., Metal–Organic Frameworks with Reduced Hydrophilicity for Postcombustion CO_2 Capture from Wet Flue Gas. *ACS Sustain. Chem. Eng.* **2018,** *6* (9), 11904-11912.
28. Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J.; Walton, K. S., Effect of Water Adsorption on Retentionof Structure and Surface Area of Metal–Organic Frameworks. *Ind. Eng. Chem. Res.* **2012,** *51* (18), 6513-6519.
29. Burtch, N. C.; Jasuja, H.; Walton, K. S., Water Stability and Adsorption in Metal–Organic Frameworks. *Chem. Rev.* **2014,** *114* (20), 10575-10612.
30. Zhang, W.; Hu, Y.; Ge, J.; Jiang, H.-L.; Yu, S.-H., A Facile and General Coating Approach to Moisture/Water-Resistant Metal–Organic Frameworks with Intact Porosity. *J. Am. Chem. Soc.* **2014,** *136* (49), 16978-16981.
31. Decoste, J. B.; Denny, J. M. S.; Peterson, G. W.; Mahle, J. J.; Cohen, S. M., Enhanced Aging Properties of HKUST-1 in Hydrophobic Mixed-Matrix Membranes for Ammonia Adsorption. *Chem. Sci.* **2016,** *7* (4), 2711-2716.
32. Kitao, T.; Zhang, Y.; Kitagawa, S.; Wang, B.; Uemura, T., Hybridization of MOFs and Polymers. *Chem. Soc. Rev.* **2017,** *46* (11), 3108-3133.
33. Ma, X.; Chai, Y.; Li, P.; Wang, B., Metal–Organic Framework Films and Their Potential Applications in Environmental Pollution Control. *Acc. Chem. Res.* **2019,** *52* (5), 1461-1470.
34. Kalaj, M.; Bentz, K. C.; Ayala, S.; Palomba, J. M.; Barcus, K. S.; Katayama, Y.; Cohen, S. M., MOF-Polymer Hybrid Materials: From Simple Composites to Tailored Architectures. *Chem. Rev.* **2020**. **DOI:** 10.1021/acs.chemrev.9b00575.
35. Yang, S.; Peng, L.; Sun, D. T.; Asgari, M.; Oveisi, E.; Trukhina, O.; Bulut, S.; Jamali, A.; Queen, W. L., A New Post-Synthetic Polymerization Strategy Makes Metal–Organic Frameworks More Stable. *Chem. Sci.* **2019,** *10* (17), 4542-4549.
36. Chen, Y.; Li, S.; Pei, X.; Zhou, J.; Feng, X.; Zhang, S.; Cheng, Y.; Li, H.; Han, R.; Wang, B., A Solvent-Free Hot-Pressing Method for Preparing Metal–Organic-Framework Coatings. *Angew. Chem. Int. Ed.* **2016,** *55* (10), 3419-3423.
37. Agostoni, V.; Horcajada, P.; Noiray, M.; Malanga, M.; Aykaç, A.; Jicsinszky, L.; Vargas-Berenguel, A.; Semiramoth, N.; Daoud-Mahammed, S.; Nicolas, V.; Martineau, C.; Taulelle, F.; Vigneron, J.; Etcheberry, A.; Serre, C.; Gref, R., A "Green" Strategy to Construct Non-Covalent, Stable and Bioactive Coatings On Porous MOF Nanoparticles. *Sci. Report.* **2015,** *5* (1), 7925.
38. Fernandez, C. A.; Nune, S. K.; Annapureddy, H. V.; Dang, L. X.; Mcgrail, B. P.; Zheng, F.; Polikarpov, E.; King, D. L.; Freeman, C.; Brooks, K. P., Hydrophobic and Moisture-Stable Metal–Organic Frameworks. *Dalt. Trans.* **2015,** *44* (30), 13490-13497.
39. Das, S.; Kumar, S.; Samal, S. K.; Mohanty, S.; Nayak, S. K., A Review on Superhydrophobic Polymer Nanocoatings: Recent Development and Applications. *Ind. Eng. Chem. Res.* **2018,** *57* (8), 2727-2745.
40. Sholl, D. S.; Lively, R. P., Seven Chemical Separations to Change the World. *Nature* **2016,** *532* (7600), 435-437.
41. Elsaidi, S.; Venna, S.; Mohamed, M. H.; Gipple, M.; Hopkinson, D., Dual-Layer MOF Composite Membranes with Rationally Tuned Interface Interaction for Post-Combustion CO_2 Separation. **2019**, *1*, 5, 10059.
42. Zhu, G.; O'Nolan, D.; Lively, R. P., Molecularly Mixed Composite Membranes: Challenges and Opportunities. *Chem. Euro. J.* **2019,** *26*, 16, 3464-3473.
43. Liu, G.; Chernikova, V.; Liu, Y.; Zhang, K.; Belmabkhout, Y.; Shekhah, O.; Zhang, C.; Yi, S.; Eddaoudi, M.; Koros, W. J., Mixed Matrix Formulations with MOF Molecular Sieving for Key Energy-Intensive Separations. *Nat. Mater.* **2018,** *17* (3), 283-289.
44. Liechty, W. B.; Kryscio, D. R.; Slaughter, B. V.; Peppas, N. A., Polymers for Drug Delivery Systems. *Ann. Rev. Chem. Biomole. Eng.* **2010,** *1* (1), 149-173.
45. Elsaidi, S. K.; Mohamed, M. H.; Schaef, H. T.; Kumar, A.; Lusi, M.; Pham, T.; Forrest, K. A.; Space, B.; Xu, W.; Halder, G. J.; Liu, J.; Zaworotko, M. J.; Thallapally, P. K., Hydrophobic Pillared Square Grids for Selective Removal Of CO_2 from Simulated Flue Gas. *Chem. Commun.* **2015,** *51* (85), 15530-15533.
46. Scott, H. S.; Ogiwara, N.; Chen, K.-J.; Madden, D. G.; Pham, T.; Forrest, K.; Space, B.; Horike, S.; Perry IV, J. J.; Kitagawa, S.; Zaworotko, M. J., Crystal Engineering of a Family of Hybrid Ultramicroporous Materials Based Upon Interpenetration and Dichromate Linkers. *Chem. Sci.* **2016,** *7* (8), 5470-5476.
47. Chen, K.-J.; Scott, H. S.; Madden, D. G.; Pham, T.; Kumar, A.; Bajpai, A.; Lusi, M.; Forrest, K. A.; Space, B.; Perry IV, J. J., Benchmark C_2H_2/CO_2 and CO_2/C_2H_2 Separation by Two Closely Related Hybrid Ultramicroporous Materials. *CHEM,* **2016,** *1* (5), 753-765.

48. Waite, M.; Cohen, E.; Torbey, H.; Piccirilli, M.; Tian, Y.; Modi, V., Global Trends in Urban Electricity Demands for Cooling and Heating. *Energy* **2017,** *127*, 786-802.
49. Li, L.; Wen, H.-M.; He, C.; Lin, R.-B.; Krishna, R.; Wu, H.; Zhou, W.; Li, J.; Li, B.; Chen, B., A Metal–Organic Framework with Suitable Pore Size and Specific Functional Sites for the Removal of Trace Propyne From Propylene. *Angew. Chem. Int. Ed.* **2018,** *130* (46), 15403-15408.
50. Belmabkhout, Y.; Bhatt, P. M.; Adil, K.; Pillai, R. S.; Cadiau, A.; Shkurenko, A.; Maurin, G.; Liu, G.; Koros, W. J.; Eddaoudi, M., Natural Gas Upgrading using a Fluorinated MOF with Tuned H_2S and CO_2 Adsorption Selectivity. *Nat. Energ.* **2018,** *3* (12), 1059-1066.
51. Cadiau, A.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Pillai, R. S.; Shkurenko, A.; Martineau-Corcos, C.; Maurin, G.; Eddaoudi, M., Hydrolytically Stable Fluorinated Metal-Organic Frameworks for Energy-Efficient Dehydration. *Science* **2017,** *356* (6339), 731-735.
52. Mukherjee, S.; Sikdar, N.; O'Nolan, D.; Franz, D. M.; Gascón, V.; Kumar, A.; Kumar, N.; Scott, H. S.; Madden, D. G.; Kruger, P. E.; Space, B.; Zaworotko, M. J., Trace CO_2 Capture by an Ultramicroporous Physisorbent with Low Water Affinity. *Sci. Adv.* **2019,** *5* (11), Eaax9171.
53. Chen, K.-J.; Madden, D. G.; Mukherjee, S.; Pham, T.; Forrest, K. A.; Kumar, A.; Space, B.; Kong, J.; Zhang, Q.-Y.; Zaworotko, M. J., Synergistic Sorbent Separation for One-Step Ethylene Purification from a Four-Component Mixture. *Science* **2019,** *366* (6462), 241-246.
54. Lu, X.; Huang, C.; Lowinger, M. B.; Yang, F.; Xu, W.; Brown, C. D.; Hesk, D.; Koynov, A.; Schenck, L.; Su, Y., Molecular Interactions in Posaconazole Amorphous Solid Dispersions from Two-Dimensional Solid-State NMR Spectroscopy. *Molec. Pharm.* **2019,** *16* (6), 2579-2589.
55. Myers, A.; Prausnitz, J. M., Thermodynamics of Mixed-Gas Adsorption. *AIChE* **1965,** *11* (1), 121-127.
56. O'Nolan, D.; Kumar, A.; Zaworotko, M. J., Water Vapor Sorption in Hybrid Pillared Square Grid Materials. *J. Am. Chem. Soc.* **2017,** *139* (25), 8508-8513.


CO2
N2
H2O
SIFSIX-3-Ni
HPMCP/SIFSIX-3-Ni
OR
RO
R
R = H, CH3 or
CH3
n
H
CH2
O
x